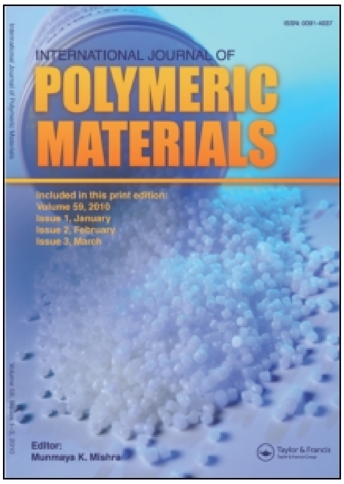

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Conducting Composites of Polymethylmethacrylate with Acetylene Black

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Conducting composites of polymethylmethacrylate and acetylene black were prepared via potassium chromate–sodium arsenite initiated redox polymerization of methylmethacrylate in presence of a suspension of acetylene black in aqueous methanol medium at 60°C. Prolonged extraction of the composite by tetrahydrofuran failed to extract the polymethylmethacrylate completely from the acetylene black surface, as confirmed by Fourier Transform Infrared studies. Scanning electron microscopic analyses revealed the formation of agglomerates of particles of nonuniform sizes and shapes. Thermal stability of the composite was appreciably improved relative to that for the unmodified base polymer. In sharp contrast to the d.c. conductivity of polymethylmethacrylate homopolymer (10^{-13} S/cm), the conductivity of the composites reached values between 10^{-4} S/cm to 10^{-2} S/cm corresponding to acetylene black loading of 7% to 25%.

Keywords: polymethylmethacrylate, acetylene black, composite, K_2CrO_4–$NaAsO_2$ redox system, thermal stability, conductivity

INTRODUCTION

During recent times synthesis of composite materials often involved as one of the components speciality polymers like polypyrrole (PPY), polyaniline (PANI), and polythiophene (PTP), which are well known for their conductivity and other optoelectronic characteristics [1].

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Use of conventional vinyl polymers like polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), polystyrene (PS), polyacrylamide (PAA), and so on was somewhat restricted because of the limited bulk properties of these polymers. However, considerable scope exists to modify these polymers with a view to enhancing their usability as advanced materials. A widely investigated method in this direction involves the preparation of conducting polymer blends and composites of the speciality conducting polymers such as PPY, PANI, and PTP with conventional polymers like PAN, PMMA, PS, and so on. Several workers [2–3] reported on the preparation of conducting polymeric blends/composites of PPY-PVC and PPY-PMMA via electrochemical and oxidative polymerization methods, respectively. Stanke et al. [4] synthesized a conducting graft copolymer film of PMMA and PPY by oxidative polymerization of PY with $FeCl_3$. Rukenstein described [5–6] preparation and evaluation of PANI/poly(alkylmethacrylate) and PPY/poly(alkylmethacrylate) composites with high electrical conductivity (6 S/cm).

In this context, the authors recently achieved [7] the preparation of water dispersible conducting ($\sim 10^{-4}$ S/cm) nanocomposites of PAN with PPY/PANI by polymerizing a mixture of AN and PY/ANI in aqueous medium by K_2CrO_4–$NaAsO_2$ redox initiators (for AN) in presence of nanosized SiO_2 as particulate dispersants. Chen et al. [8] also prepared gel polymer nanocomposite electrolyte based on PMMA, clay mineral, ethylene carbonate (EC), and $LiClO_4$ that possessed high ionic conductivity ($\sim 10^{-3}$ S/cm).

In an alternative process, blending of polymers with conducting fillers, such as natural graphite flake, carbon black, and powders, to prepare electrically conducting composites was attempted in the past few decades. In this context, Chen et al. [9] prepared conducting PMMA/graphite nanosheet composites via in situ polymerization of methylmethacrylate (MMA) by benzoyl peroxide in aqueous alcohol solution in presence of expanded graphite (EG). The authors recently reported [10] that acetylene black (AB) the purest form of highly conducting carbon black was capable of initiating the polymerization of N-vinylcarbazole. Interestingly, this system led to the simultaneous formation of a PNVC-AB composite with a conductivity in the order of 10^{-2} S/cm. Earlier, Japanese groups reported [11–16] the polymerization of vinyl monomers like styrene, α-methylstyrene, iso-butylvinylether, N-vinyl-2-pyrrolidone in the presence of carbon black (CB) and an external catalyst, causing the formation of graft composites in the systems. Biwas et al. [17–20] also explored the initiation of the polymerization of NVC by Orient black (N220), Vulcan XC-72, and so on without any external oxidant.

With this in mind, this article describes a novel procedure for the preparation of a conducting PMMA-AB composite via K_2CrO_4–$NaAsO_2$ initiated redox polymerization of MMA in aqueous-alcoholic medium, and highlights some relevant bulk properties of the PMMA-AB composite.

EXPERIMENTAL

Materials and Methods

Methylmethacrylate, Merck–Schuchardt (99%), stabilized with 100 ppm hydroquinone was washed with a small amount of sodium hydroxide solution (10%). The monomer was dried over anhydrous sodium sulphate, and finally fractionated. Acetylene Black (SENCO, Chennai, India) was preheated by heating at 120°C for 2 h in vaccum prior to use. Potassium chromate (Riedel, Germany) and sodium arsenite (Riedel) were used as the oxidant and the reductant, respectively. All solvents were of analytical grade and were freshly distilled before used.

Polymerization of Methylmethacrylate with K_2CrO_4–$NaAsO_2$ Redox System

0.1 g of K_2CrO_4 was dissolved in 30 ml of distilled water in a Pyrex flask to which 1.5 ml of methylmethacrylate was injected. The system was kept stirring at 60°C under N_2 atmosphere for 10 min and thereafter, 0.3 g of $NaAsO_2$ was dissolved into this solution. Then the total system was kept at room temperature for 6 h. Thereafter, the white polymer was centrifuged, washed in succession with distilled water, methanol, and finally dried in vacuum for 12 h.

Preparation of PMMA-AB Composite

In a Pyrex flask (0.03–0.50 g) varying amounts of AB were added to 30 ml of water-methanol mixture (3 ml methanol) under sonication for 1 h to make a suspension of AB in which 0.1 g of K_2CrO_4 was dissolved and 1.5 ml of methylmethacrylate was injected. Thereafter, 0.3 g of $NaAsO_2$ was added to it. The system was refluxed at 60°C for 6 h under N_2 atmosphere. The total black mass was washed in succession with distilled water, methanol, and finally dried in vacuum for 12 h. This mass was further extracted with THF through continuous refluxing for one week at 80°C to dissolve any PMMA homopolymer. The total content was centrifuged, a process repeated at least four times until the extract did not yield any precipitate with methanol due to any surface-adsorbed PMMA. This residue was finally dried at 80°C for 12 h under vacuum. After various physicochemical characterizations, the composite was confirmed to contain PMMA along with AB.

Characterization and Property Evaluation

The FTIR spectrum of the PMMA-AB composite was taken on a JASCO-410 instrument (Essex, UK) in pressed KBr pellet. Dispersions of PMMA-AB composite in 2-propanol were microsprayed on mica substrates. Each sample was sputter coated with gold layer and a Hitachi S-415 A (Tokyo, Japan) scanning electron micrograph was used to take the micrographs. Thermogravimetric analyses were performed on a Shimadzu DT-40 (Kyoto, Japan) instrument. Direct current (d.c.) conductivity measurements were taken on pressed pellets with silver coating, using the conventional four-probe technique.

RESULTS AND DISCUSSION

General Features of Composite Formation

Table 1 presents some results of the polymerization and composite formation of PMMA with AB. Control experiments showed that 86%

TABLE 1 Some Typical Data on Composite Formation of PMMA with AB

		Weight (g) of composite			
Entry no.	Weight (g) of AB	Before reflux with THF	After reflux with THF	% Polymer formed	% Polymer grafted per g of composite
1	0.03	1.14	0.41	80	92
2	0.04	1.10	0.50	75	92
3	0.05	1.08	0.65	73	90
4	0.10	1.08	0.70	70	85
5	0.20	1.11	0.80	65	78
6	0.30	1.14	1.00	60	70
7	0.40	1.21	1.10	58	63
8	0.50	1.27	1.15	55	56

Experimental conditions: Weight of MMA = 1.41 g, weight of K_2CrO_4 = 0.1 g, weight of $NaAsO_2$ = 0.3 g, total volume = 30 ml (water = 27 ml and MeOH = 3 ml), temperature = 60°C, time of polymerization = 6 h.

% Polymer formed in the control experiment (without AB: using same experimental conditions mentioned earlier) was 86%. % polymer in the composite = [(column 3 − column 2)/1.41] × 100.

% Grafting = [(column 4 − column 2)/column 4] × 100.

PMMA homopolymer formation was realized when the polymerization occurred in presence of K_2CrO_4 (0.1 g) and $NaAsO_2$ (0.3 g) in water medium without any AB. Entries 1–8 indicate that the percentage conversion to PMMA homopolymer decreased with increasing weight of AB at fixed amount of redox system and monomer in the initial feed. After prolonged extraction of PMMA-AB composites with THF at 80°C, some residual amount of PMMA (column 4, Table 1) was found to be present in the PMMA-AB composite. A similar observation was made by the present authors [21] in the PAN-AB composite system. Recently they reported [22] that the polymerization of acrylonitrile by K_2CrO_4–$NaAsO_2$ redox system occurred via a free radical pathway according to the following reactions:

$$NaAsO_2 + H_2O = NaHAsO_3 \text{ [Reference 23]}$$

$$H_2AsO_3^- + Cr^{6+} = HAsO_3^\bullet + Cr^{5+} \text{ [Reference 24]}$$

Accordingly, the following scheme is suggested for the MMA-Cr^{6+}/ $NaAsO_2$ polymerization system:

Initiation

$$H_2AsO_3^\bullet + CH_2{=}CH(Me){-}COOMe \rightarrow H_2AsO_3{-}CH_2{-}C^\bullet H(Me){-}COOMe$$

Propagation

$$H_2AsO_3{-}CH_2{-}C^\bullet H(Me){-}COOMe + nCH_2{=}CH(Me){-}COOMe$$

$$\longrightarrow H_2AsO_3{-}(CH_2{-}CH(Me){-}COOMe)_n{-}CH_2{-}C^\bullet H(Me){-}COOMe$$

The formation of PMMA-AB composite with some residual non-extractable PMMA is reminiscent of the situation recently encountered by the authors in the PAN-AB composite system [21]. In the latter case they proposed that growing PAN moieties in the system containing free radicals could couple with the free radical centers known to be present in conducting grades of carbon black [11–21]. It is believed that a similar mechanism is also operative in the PMMA-AB composite formation process as proposed schematically later in this article.

In this context, it is relevant to recall recent observations [10,25] that AB and fullerene were capable of directly initiating polymerization of NVC without any external initiator via electron transfer reaction between lone pair of nitrogen of NVC and the free electrons in AB or fullerene. The authors' contention was subsequently endorsed by Chen et al. [26] by ESR studies in NVC$-C_{60}$ polymerization system. Biswas et al. [17–20] reported earlier that conducting grades of CB, Orient black (N220), Vulcan XC-72, and so on were also able to initiate NVC polymerization without any external initiator, apparently through charge transfer reaction between N lone pair in NVC and free radicals present in carbon black.

In the present particular system the authors failed to obtain any PMMA-AB graft composite from the interaction of preformed PMMA and AB suspension. The PMMA-AB composite was obtained only during in-situ polymerization of MMA in presence of AB suspension and the redox system. On the basis of these observations it is felt that the following grafting mechanism is fairly reasonable:

$$H_2AsO_3-(CH_2-CH(Me)-COOMe)n-CH_2-C^{\bullet}H(Me)-COOMe + AB^{\bullet}$$
$$\longrightarrow H_2AsO_3-(CH_2-CH(Me)-COOMe)_n-CH_2-CH(Me)(COOMe)-AB$$

^{1}H NMR Studies of PMMA Homopolymer

The ^{1}H NMR spectrum of the resulting PMMA homopolymer obtained via K_2CrO_4–$NaAsO_2$ redox polymerization revealed signals at 0.93–1.23 ppm due to the protons of methyl group of $-C(CH_3)(COOCH_3)$, the signals from 1.90–2.5 are attributed to the methylene group of $-CH_2-$, and the peaks at 3.1–3.56 ppm correspond to the methoxy groups in the main chain. These peaks matched with the reported ^{1}H NMR peaks of PMMA homopolymer prepared by Wang et al. [27] via reverse atom transfer radical polymerization of MMA with $FeCl_3$/pyromellitic acid.

FTIR Absorption Characteristics of PMMA-AB Composite

Table 2 shows the characteristic band positions and assignments for PMMA-AB composite. The presence of PMMA in the PMMA-AB composite recovered after repeated extraction with THF was supported by the appearance of FTIR peaks (cm^{-1}) at 1729, 1475, 1445, 1385, 1266, 1236, 1186, 1136, 1062, 992, 962, 837, 748, which correlated closely with the corresponding peaks reported in the FTIR spectra of the PMMA homopolymer [28].

Scanning Electron Micrographic Characterization

Figures 1(a)–(c) present the scanning electron micrographs for AB, PMMA homopolymer, and PMMA-AB composite, respectively.

TABLE 2 FTIR Absorption Characteristics of PMMA-AB Composite

Peaks (cm^{-1})	Assignments
1729	$\nu(C{=}O)$
1475	$\delta(CH_2)_b$
1445	$\delta(CH_3)_b$
1385	$\delta(CH_3)_b$
1266	$\nu(CO)$
1236	$\nu(CO)$
1186	$\nu(COC)$
1136	$\nu(COC)$
992	$\delta(CH_3)_r$
962	$\delta(CH_3)_r$
837	$\delta(CH_2)_r$
748	$\delta(CH_3)_r$

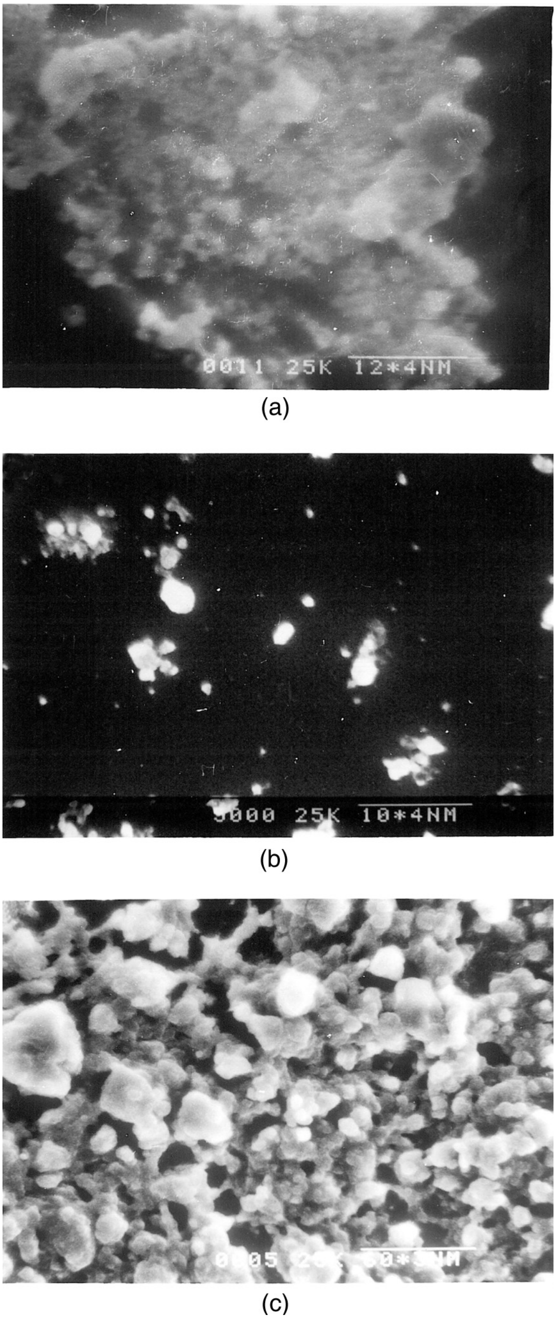
The SEM morphology for AB showed the presence of small nearly spherical AB particles with the tendency to form larger lumps (40 nm) randomly distributed on the surface. The morphology for PMMA homopolymer indicated the formation of lumpy aggregates of mixed sizes ranging from 15–60 nm with definite pattern. In contrast, SEM photograph of the PMMA-AB composite suggested the formation of lumpy agglomerates of much larger particles with nonuniform sizes and shapes. The formation of such microaggregates could result through cementation of nanosized AB particles with the precipitating PMMA homopolymer—a situation similar to the scenario described by Armes et al. [29] in their polymer-metal oxide nanocomposite systems where the nanocomposites were considered to be made up of microaggregates "glued" [30] together by the precipitating polymer component. In the light of this concept the high conductivity of the PMMA-AB composite is consistent with the compact interparticle morphology observed in the PMMA-AB composite.

XRD Analysis

The XRD analyses for PMMA-AB composite and PMMA homopolymer showed a completely amorphous pattern.

Thermal Stability Characterization

TGA (Figure 2) studies revealed that the overall thermal stability followed the trend: AB > PMMA-AB > PMMA. Incorporation of AB



(a)

(b)

(c)

FIGURE 1 Scanning electron micrographs of (a) AB, (b) PMMA homopolymer, and (c) PMMA-AB composite.

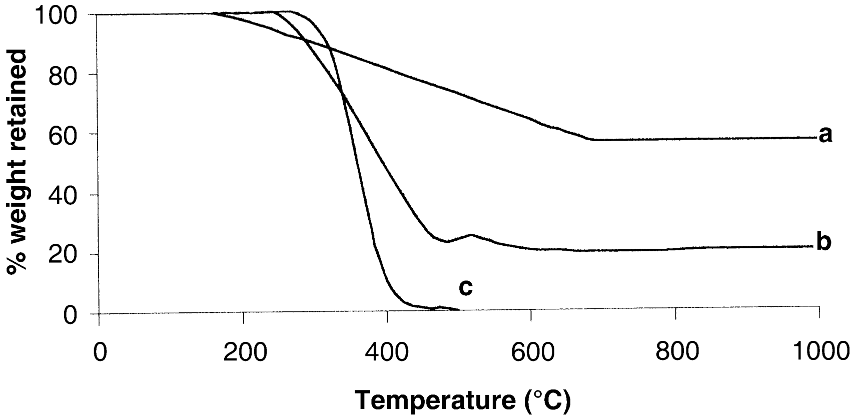


FIGURE 2 TGA of (a) AB, (b) PMMA-AB composite, and (c) PMMA homopolymer.

moieties of higher thermal stability in the PMMA-AB composite would be expected to enhance the stability of the base polymer in the composite. A similar trend was also reported for a variety of polymer-metal oxide/clay nanocomposite systems [31–36].

Figure 2 reveals that at 420°C, PMMA homopolymer was lost completely. However, in this temperature range the PMMA-AB composite (entry 7, Table 1) underwent 75% loss in weight whereas AB suffered 20% loss in weight. Consequently, it could be assumed the % of residual PMMA in the composite was (75−20)% or 55%. This value in fairly close to actual polymer loading in the composite used (last column of entry 7, Table 1). Such a procedure was used by Armes et al. [29] and by the present authors [37–38] in gaining information about polymer loading from thermal stability data in polymer-metal oxide nanocomposite systems.

DTA scan of PMMA-AB composite exhibited an endothermic peak at 400°C in the PMMA-AB composite, which was absent in the PMMA homopolymer DTA scan. Again, an exothermic peak at 457°C was detected in the DTA scan of PMMA homopolymer, which was not present in the PMMA-AB system. The endothermic peak could originate from endothermic bond breaking process in the PMMA-AB graft structure. The DTA scan of PMMA-AB composite further revealed a strong exothermic peak at 582°C, which was not present in the DTA scan for PMMA but was prominently displayed in the DTA scan for AB. The observed DTA peak at 582°C for AB was possibly due to oxidative degradation of various functional groups (−OH, −COOH, >C=O,

TABLE 3 Conductivity Values of PMMA Based Composites with PMMA Homopolymer

Entry no.	Materials	Conductivity (S/cm)	Reference
1	PMMA (0% AB content)	10^{-13}	[9,28,39]
2	PMMA-AB (7% AB content)	1.2×10^{-4}	this study
3	PMMA-AB (8% AB content)	1.5×10^{-5}	this study
4	PMMA-AB (14% AB content)	2.1×10^{-2}	this study
5	PMMA-AB (25% AB content)	6×10^{-2}	this study
6	PMMA-NanoG	10^{-3}	[9]
7	PMMA/PPY composite film	12×10^{-2}	[4]
8	PMMA-PPY composite (depending on weight % of PPY content)	10^{-9}-10^{-1}	[28]
9	PMMA-Li(ClO_4)-EC/Dclay nanocomposite	10^{-3}	[8]

–CHO, etc.) believed to be present in various types of carbon blacks [14,16].

Conductivity Characteristics

Table 3 presents the d.c. conductivity values of PMMA homopolymer and of some PMMA-based composites. Several workers reported that the bulk conductivity of pure PMMA was in the order of 10^{-13} S/cm [9,28,39]. Interestingly, the PMMA-AB composite exhibited attractively high conductivity values relative to that for the base polymer, which increased with increasing weight percentage of AB in the composite. Thus, at 14 percent AB content, the conductivity increased by $\sim 10^9$-fold relative to that of PMMA homopolymer while the value progressively increased by 10^2-fold corresponding to a 4-fold increase in the percentage of AB loading in the PMMA-AB composite. This feature is quite consistent with the reported conductivity enhancement of polymers blended with conductive fillers [9].

CONCLUSION

Conducting composites of PMMA-AB were prepared via K_2CrO_4–$NaAsO_2$ redox initiated polymerization of MMA in presence of AB suspension in aqueous-alcohol dispersions. The conductivity of the PMMA-AB composite containing 25% of AB was improved 10^{11} times higher than that of PMMA homopolymer.

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